

## Novel Mercury (II) complexes of Schiff base ligands: Synthesis, spectral Characterization.

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### ABSTRACT

Mercury (II) complexes were synthesized with Schiff base ligands,  $[\text{HgL}_2\text{Cl}_2]$  ( $\text{L}^1 = \text{bis}(\text{acac})\text{-O-Phenylene diamine}$ ) and  $\text{L}^2 = \text{bis}(1\text{-Phenylbutane-1,3-dione})\text{Phenylene diamine}$ ] are described. These complexes were characterized by elemental analysis, molar conductance, magnetic susceptibility measurements, IR, electronic spectral studies and  $^1\text{H-NMR}$  spectral studies. The molar conductance measurements of complexes in DMF correspond to 1:2 electrolytes. On the basis of above observation the complexes were proposed to be octahedral in nature. The changes observed between the FT-IR and UV-VIS spectra of the ligands and the complexes allowed us to establish the co-ordination mode of the metal in complexes. The results suggest that the Schiff bases coordinate as divalent anions with their two dentate N donors derived from the carbonyl and azomethine nitrogen.

**Keywords:** Mercury, complexes, Schiff base ligands, synthesis, characterization.

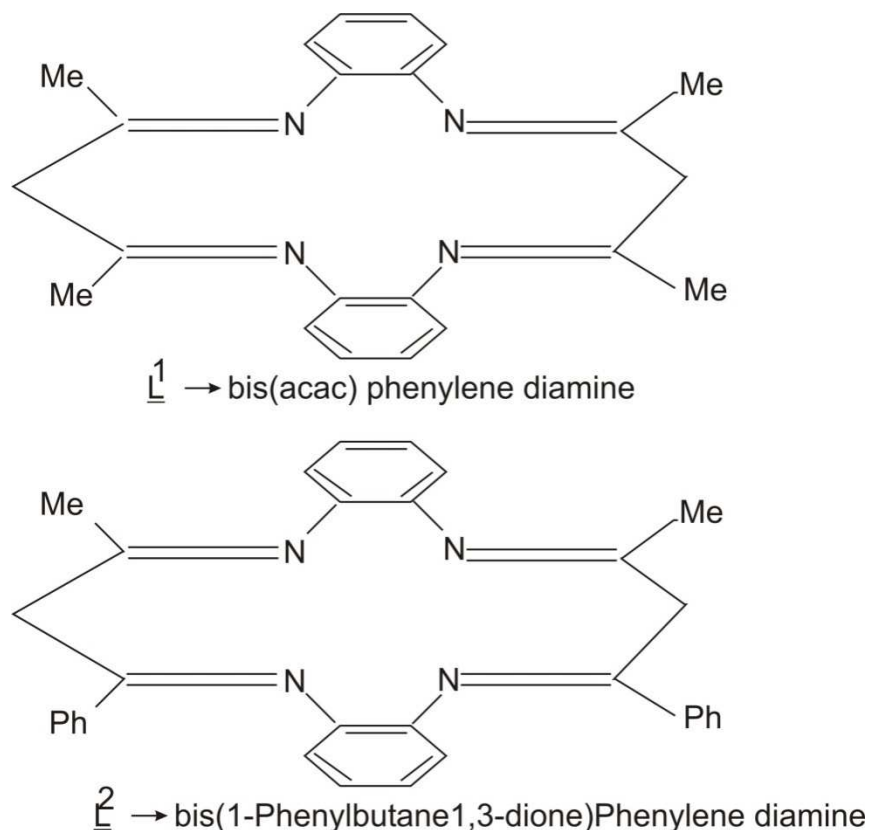
### INTRODUCTION

Metal complexes play an essential role in agriculture, Pharmaceutical and industrial chemistry. Ligand, a metal surrounded by a cluster of ions or molecule, is used for the preparation of complex compounds known as Schiff bases<sup>1</sup>, which are condensation products of primary amines with active carbonyls. ( $\text{RCH}=\text{NR}^1$ , where R &  $\text{R}^1$  represents alkyl / or aryl

substituents). The development of the field of bioinorganic chemistry has increased the interest in Schiff base complexes, Since it has been recognized that many of these complexes may serve as models for biologically important species (2-6). Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer and herbicidal applications (7-8). The coordination

chemistry of Mercury (II) differs from most other transition metals due to its large size and  $d^{10}$  configuration. Its interference in biological systems, and its potential as a toxin or as a medicine has required a better understanding of its coordinative properties (9-10). In this

work, we report the synthesis and structural studies of the complexes isolated from the reaction of mercury (II) halide with bis (acetyl acetone) orthophenylene- diamine ( $L^1$ ) and bis (1-Phenyl butane 1,3-dione) ortho phenylene diamine ( $L^2$ ) (fig 1)



## MATERIAL AND METHODS

All the reagents were supplied by Merck and were used without further purification. Melting points of the complexes were determined in a Electro thermal 9200. The elemental analysis for C, H and N were determined in a semi micro scale at SAIF, C. D. R. I. Lucknow.

Conductance of the complexes were measured at room temperature in DMF and DMSO by Elico Conductivity Bridge. The Infrared spectra of the complexes and ligands were recorded the range (4000-650  $\text{cm}^{-1}$ ) on Perkin-Elmer 457 spectrometer at room temperature in KBr (for complexes) or in nujol (for ligands)  $^1\text{H}$ NMR spectra in

$\text{CDCl}_3$  and DMSO were recorded on NMR spectrophotometer. Electronic spectra in methanol were recorded on Perkin-Elmer lambda-2B spectrophotometer.

### Synthesis of Schiff base ligands

The Schiff bases were synthesized by adding the methanolic solution of acac/1-Phenyl butane 1,3-dione) (0.01 mol) to the alcoholic solution of O-Phenylene diamine (0.01 mol) in equimolar ratio. The reaction mixture was then refluxed on a water bath for about 4-7 hrs. The condensation product was thoroughly washed, recrystallized, dried and characterized. The purity of the synthesized compounds was monitored by TLC, using silica gel as an adsorbent.

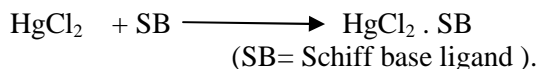
### Preparation of metal complexes

The metal complexes have been synthesized by mixing the methanolic solution of the  $\text{HgCl}_2$  (0.01 mol) to the methanolic solution of ligand (0.01 mol) in 1:1 molar ratio and the resulting mixture was refluxed on water bath for 3-6 hrs. A colored product appeared on standing and cooling the above solution. It was filtered washed and dried under reduced pressure over anhydrous  $\text{CaCl}_2$  in a desiccators followed by heating (60-80°C) in an electric oven.

## RESULTS AND DISCUSSION

The complexes [ bis (acac) Phenylene diamine]  $\text{Hg}(\text{II})$  and [ bis (1-Phenyl butane 1,3-dione) Phenylene diamine]  $\text{Hg}(\text{II})$  were prepared in good yield by stirring stoichiometric amounts of  $\text{HgCl}_2$  and  $\text{L}^1$  and  $\text{L}^2$  (fig 1). The analytical data (Table1) of the complexes show that they have metal to ligand stoichiometric in 1:2

ratios. The molar conductance values of the complexes of  $\text{Hg}(\text{II})$  with  $\text{L}^1$  and  $\text{L}^2$  ligands in acetone  $10^{-3}\text{M}$  suggest their non-electrolytic nature<sup>11</sup> with composition of  $\text{HgX}_2\cdot\text{SB}$ . The representative equation of synthesis of complexes is shown below:



The complexes were characterized by the usual methods: elemental analysis, FTIR,  $^1\text{H}$ NMR, absorption electronic spectroscopy. All these molecular adducts are stable towards atmospheric oxygen and moisture. All complexes were stable at room temperature even on long standing. All these complexes are soluble in organic solvents such as DMSO and DMF but insoluble in water.

### Structure Interpretation

#### IR Spectra

The infrared spectra of the complexes taken in the region 4000 – 650  $\text{cm}^{-1}$  and in few cases in the region 4000 – 200  $\text{cm}^{-1}$  in CsI. ( IR spectra of ligands were recorded in nujol). There are some significant changes between the metal (II) complexes and their free ligands chelation as expected. The main stretching frequencies of the IR spectra of the ligands ( $\text{L}^1 - \text{L}^2$ ) and their metal complexes are tabulated in table 2. An exhaustive comparison of the IR spectra of the ligands and complexes gave information about the mode of bonding of the ligands in metal complexes. The IR spectra of  $[\text{HgL}_2]\text{Cl}_2$  complexes, the ligands act as a neutral tetradentate through the azomethine and carbonyl group<sup>12</sup>. All these  $\text{Hg}(\text{II})$  complexes exhibit the  $\nu \text{C}=\text{N}$

absorption band around 1620-1610  $\text{cm}^{-1}$  which normally appears at 1640  $\text{cm}^{-1}$  to 1650  $\text{cm}^{-1}$  in the free ligand<sup>(13-14)</sup>. The lowering of this band in these complexes indicate the co-ordination of nitrogen atoms

of azomethine groups to the mercury ion<sup>(15)</sup>. The far IR exhibited bands at 420-390  $\text{cm}^{-1}$  and 255—210  $\text{cm}^{-1}$  for  $\nu$  Hg-N and  $\nu$ Hg-Cl<sup>(16-17)</sup> respectively.

**Table 1 The physical and analytical data of the ligands and complexes.**

Compound	Molecular Formula	Mol.wt.	M. P. °C	solubility	Elemental analysis found (calc.)				Molar Conductance in acetone ( $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ )	$\mu_{\text{eff}}$ . (BM)
					%C	%H	%N	%M		
L <sup>1</sup>	C <sub>22</sub> H <sub>22</sub> N <sub>4</sub>	342	180°C	DMF	45.68 (45.78)	2.4 (2.7)	10.2 (10.5)	---	---	---
L <sup>2</sup>	C <sub>32</sub> H <sub>26</sub> N <sub>4</sub>	514	210°C	DMF	42.16 (42.14)	2.0 (2.2)	12.2 (12.4)	---	---	---
[1]	C <sub>22</sub> H <sub>22</sub> N <sub>4</sub> Hg Cl <sub>2</sub>	493	185°C	DMF, DMSO	43.0 (43.2)	3.4 (3.6)	9.0 (9.1)	32.3 (32.6)	25	Diamag- netic
[2]	C <sub>32</sub> H <sub>26</sub> N <sub>4</sub> Hg Cl <sub>2</sub>	617	252°C	DMF, DMSO	52.0 (52.2)	3.4 (3.5)	7.4 (7.5)	27.0 (27.1)	24	Diamag- netic

## H<sup>1</sup>NMR

In NMR spectra of complexes we observed a shift of electron density from the ligand to the metal. H<sup>1</sup>-NMR spectra of the complexes (1), (2) show all the expected signals. In all the spectra, a singlet corresponding to a single proton is observed in the range  $\delta$ 9.4, 11.4 ppm which is attributed to the azomethine proton (-HC=N) in Hg (II) complexes, respectively. The H<sup>1</sup>-NMR spectra of the [HgL<sub>2</sub>]Cl<sub>2</sub> complexes show a negative shift of the signal due to the NH group.

This signal is observed at  $\delta$ 8.9, 11.2 ppm in (1) and (2) complexes, suggesting that the coordination proceeds through the carbonyl oxygen or azomethine nitrogen groups. The signals of the aromatic protons of the ligands appeared at  $\delta$ 7.20, 7.90 and the resonance lines found correspond to the calculated multiplicity. These signals do not suffer relevant changes in the chemical shifts for the Hg (II) complexes.

**Table 2 IR spectra bands of ligands and Its metal complexes.**

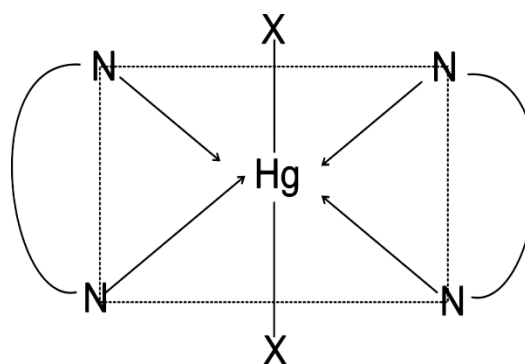
Compound	$\nu$ (N-H)	$\nu$ (C=O)	$\nu$ (C=N)	$\nu$ Hg-N	$\nu$ Hg-Cl
L <sup>1</sup>	3186	1685	1640	-----	-----
L <sup>2</sup>	3098	1686	1650	-----	-----
[1]	3186	1672	1620	420	255
[2]	3092	1678	1610	390	210

**Magnetic moment & Electronic spectra**

Electronic spectra and magnetic measurements were performed in order to obtain information about the geometry of the complexes. The formation of the ligand and Hg (II) complexes was also confirmed by UV-VIS spectra. The UV-Visible spectrum of the ligand exhibits two bands at 36630 and 29673  $\text{cm}^{-1}$ , which are assignable to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  respectively. The absorption spectra of the diamagnetic Hg (II) complexes were recorded as  $10^{-4}$  M CH<sub>3</sub>OH solutions in the range 200 – 800 nm using a quartz cuvette of 1 cm path length. The complexes show only the charge transfer transitions which can be assigned to charge transfer from the ligand to the metal and vice versa, no d-d transition are expected for  $d^{10}$  Hg (II) complexes. When compared complexes with the free ligands values have shifts frequency. The data of the spectra of the metal (II) complexes in methanol solutions are shown that absorption band observed at 278 and 318 nm is attributed to  $n \rightarrow \pi^*$  electronic transition of functional group involving the whole conjugation.

**CONCLUSION**

In this study we have reported the synthesis of new Schiff base ligands and their Hg (II) complexes. The structural characterization of synthesized compounds were made by using the elemental analysis, IR, <sup>1</sup>H NMR and UV spectral techniques. The overall experimental evidences thus show that the studied Hg (II) complexes [Hg L<sub>2</sub>] Cl<sub>2</sub> display a coordination number six and have an octahedral environment around the metal ion. From the spectroscopic characterization, it is possible to assign structure of Hg (II) complexes.



Schematic representation of metal complexes.

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